

breakable clumps or particles, which are not sticky and have a mean particle size greater than 100  $\mu\text{m}$ , usually greater than 1 mm. The term crumb in relation to this invention is defined as non-sticky particles, i.e. particles as in powders that do not stick together and remain free to each other, at least 95% of which has an average diameter 0.7-15 mm, preferably 1-7 mm.

Such crumbs are known from the process of preparing of fully aromatic polyamides based on e.g. PPD and TDC, which products are known under the trade names Twaron® (Teijin Twaron) and Kevlar® (DuPont). After polymerization in NMP/ $\text{CaCl}_2$  a crumb is obtained which can be easily coagulated, washed, and dried, and the product obtained can be dissolved in sulfuric acid and shaped into a desired form, like fibers or films.

The monomer of interest, DAPBI (5(6)-amino-2-(p-aminophenyl)-benzimidazole; CAS reg. no: 7621-86-5), is added to the diamine mixture with the objective to obtain a suitable polymer solution right after polymerization with e.g. PPD and TDC, which can be directly shaped into fibers or films, whereby DAPBI is seen as a suitable co-monomer to keep the aramid polymer in solution. It was now found that by selecting a specific ratio of PPD, DAPBI, and  $\text{CaCl}_2$  the formation of powders, paste, dough, and the like could be prevented.

To this end the invention relates to a method for obtaining a composition comprising an aromatic polyamide containing para-phenylene terephthalamide and 2-(p-phenylene)-benzimidazole terephthalamide units by copolymerizing:

- i) a mole % of para-phenylenediamine;
- ii) b mole % of 5(6)-amino-2-(p-aminophenyl)benzimidazole; and
- iii) 90-110 mole% of terephthaloyl dichloride

in a mixture of N-methyl pyrrolidone and containing c wt.% of calcium chloride, wherein c is within the range from 1 to 20, and wherein the ratio a : b ranges from 1 : 20 to 20 : 1, a + b is 100 mole%, and i), ii), and iii) together comprise 1-20 wt.% of the mixture, characterized in that the product b.c is at least 50 and less than 215 and that the composition is a crumb with a relative viscosity  $\eta_{\text{rel}}$  of at least 4, wherein the crumb is defined as non-sticky particles at least 95% of which having an average diameter of 0.7-15 mm.

It is one of the other objectives of the present invention to obtain crumbs comprising a polymer with a sufficient high relative viscosity  $\eta_{\text{rel}}$ . Relative viscosities  $\eta_{\text{rel}}$  of at least 4, more preferably between 4 and 7, most preferably at least 5 can be obtained according

to the method of the invention. It is further preferred to have a mixture for copolymerization wherein b.c is at least 80.

5 In another object of the invention a method for obtaining a purified aromatic polyamide is obtained by coagulating and washing the obtained crumb with water, followed by drying. The drying step can be performed according to standard procedures, such as ambient conditions, or at elevated temperature and/or lowered pressure. The thus obtained material is suitable for making a spin dope by dissolving it in a solvent, for instance sulfuric acid, NMP, NMP/CaCl<sub>2</sub>, dimethylacetamide, and the like. The dope can be used  
10 to manufacture formed articles, such as fibers, films, and the like.

In the following experiments, the aspects of the invention are exemplified.

#### General polymerization procedure

15 DAPBI (ex Spektr T.T.T., Russia) was dried under vacuum for 1 h at 160° C. PPD (Teijin Twaron), TDC (freshly distilled), NMP/CaCl<sub>2</sub> and NMP (both ex Teijin Twaron) were used as received (moisture content 80 ppm).

20 The glassware was pre-dried for 1 h in an air circulation oven at 120° C. A clean and dry 2 l flask was supplied with a mechanical stirrer, N<sub>2</sub>-inlet and outlet, and vacuum supply. Generally, the N<sub>2</sub>-stream is between 40 – 60 ml/min. A large part (400 ml) of the solvent and the precisely pre-weighed amines were carefully brought in the reactor. The reactor was closed and purged two times with nitrogen. The mixture was stirred for 30 min at 150  
25 rpm and heated to 60° C and mixed for 0.5 h to dissolve or disperse the amines properly. The flask was cooled with ice/water to 5 – 10° C. After removing the coolant, the stirrer velocity was set at 320 rpm and a precisely pre-weighed amount of the acid chloride was brought into the vessel through a funnel. In all cases the mol ratio of the total number of amines and the acid chloride equals one. The flask, which contained the acid chloride  
30 and the funnel, were rinsed with the remaining solvent (50 ml). The vessel was closed and the mixture was allowed to react for at least 30 min (nitrogen flush between 40 – 60 ml/min). The stirring was stopped and the reaction vessel was removed.

35 The crumbed product together with demi-water was gently added into a Condux LV15 15/N3 coagulator and the mixture was collected on an RVS filter. The product was washed 4 times with 5 l of demi-water, collected in a 2 l glass beaker and dried under vacuum for 24 h at 80° C.

Table

Examples	PPD a mole%	DAPBI b mole %	CaCl <sub>2</sub> c wt. %	b.c	$\eta_{rel}$	$\eta_{inh}$	crumb
1	90	10	10.40	104.0	6.29	6.46	yes
2	90	10	11.55	115.5	5.93	6.2 <sup>#</sup>	yes
3	80	20	9.85	197.0	5.38	5.92	yes
4	80	20	10.28	205.6	4.10	5	yes
5	60	40	4.77	190.8	5.69	6.01	yes
6	33	67	3.09	207.0	6.98	6.45	yes
7	30	70	2.82	197.4	6.2 <sup>*</sup>	6.3 <sup>#</sup>	yes
Comparative Examples							
I	80	20	11.55	231.0	4.59	5.3 <sup>#</sup>	dough/paste
II	60	40	5.49	219.6	5.87	6.2	dough/paste
III	33	67	4.56	306.9	2.75	3.58	dough/paste
IV	33	67	2.88	193.0	2.31	3.04	gel <sup>*</sup>
V	80	20	1.96	39.2	1.56	1.93	powder

average of 3 values

<sup>#</sup> calculated value<sup>\*</sup> gel with precipitated particles

The Table shows the advantageous properties when the conditions of the invention are satisfied. For instance Comparative example V (according to US 4,172,938) has a product b.c value outside the claimed range (39.2) and a relative viscosity below 4 (1.56). No crumb is formed, but a powder (having a particle size far below the average diameter 0.7 mm).